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D6C8

(56) Documents cited  
GB 2208168 A GB 2197340 A GB 2179364 A  
GB 2178754 A GB 2178055 A GB 2176799 A  
GB 2172897 A GB 2118963 A EP 0034387 A2

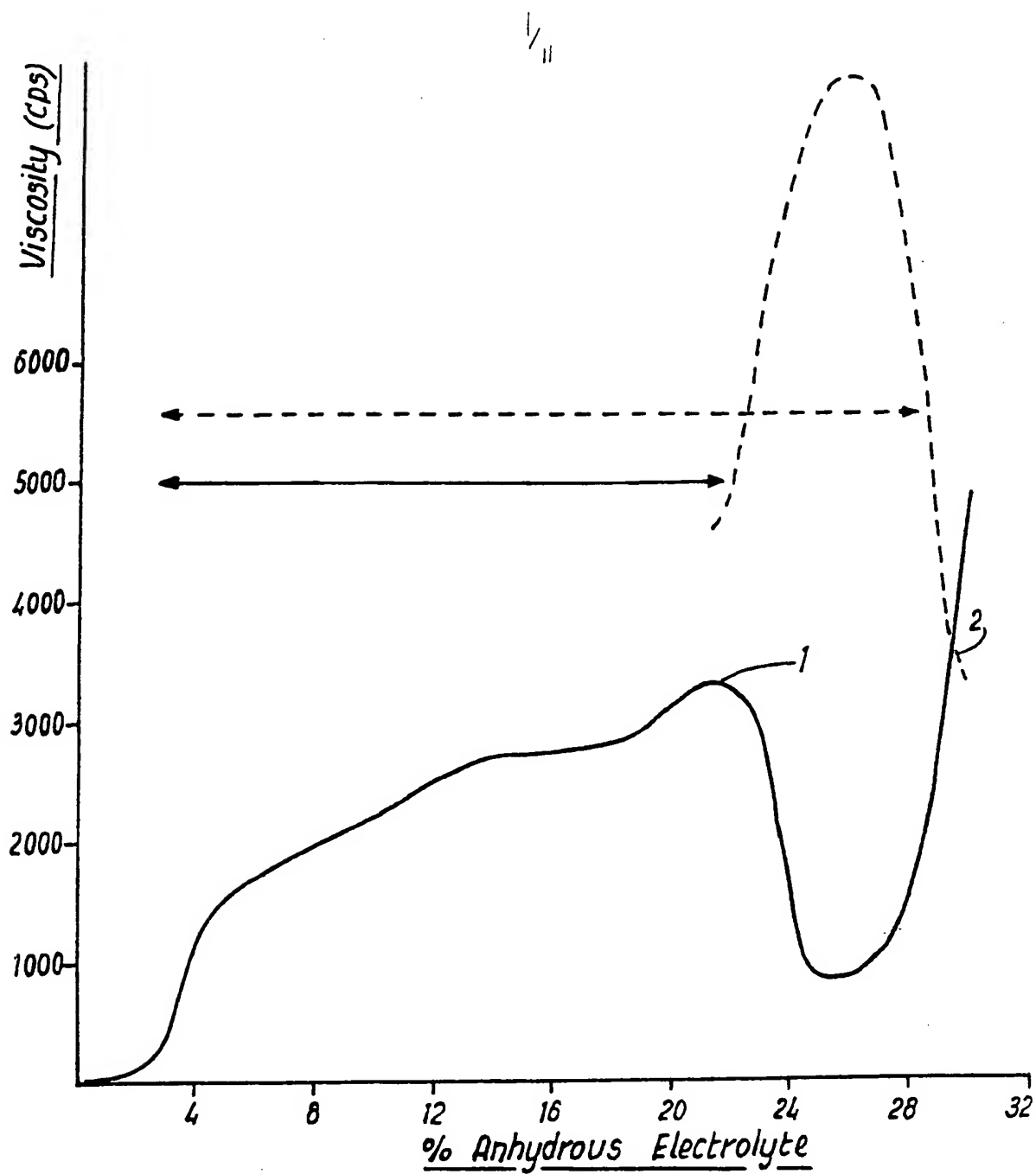
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UK CL (Edition J) C5D  
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(54) Detergent composition

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(57) A detergent composition comprising a builder, a surfactant, and an electrolyte, the level of the electrolyte being such that the surfactant is neither present in a spherulitic phase nor a lamellar phase. The composition is stabilised by a mineral silicate such as bentonite clay.

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**FIG. 1a**

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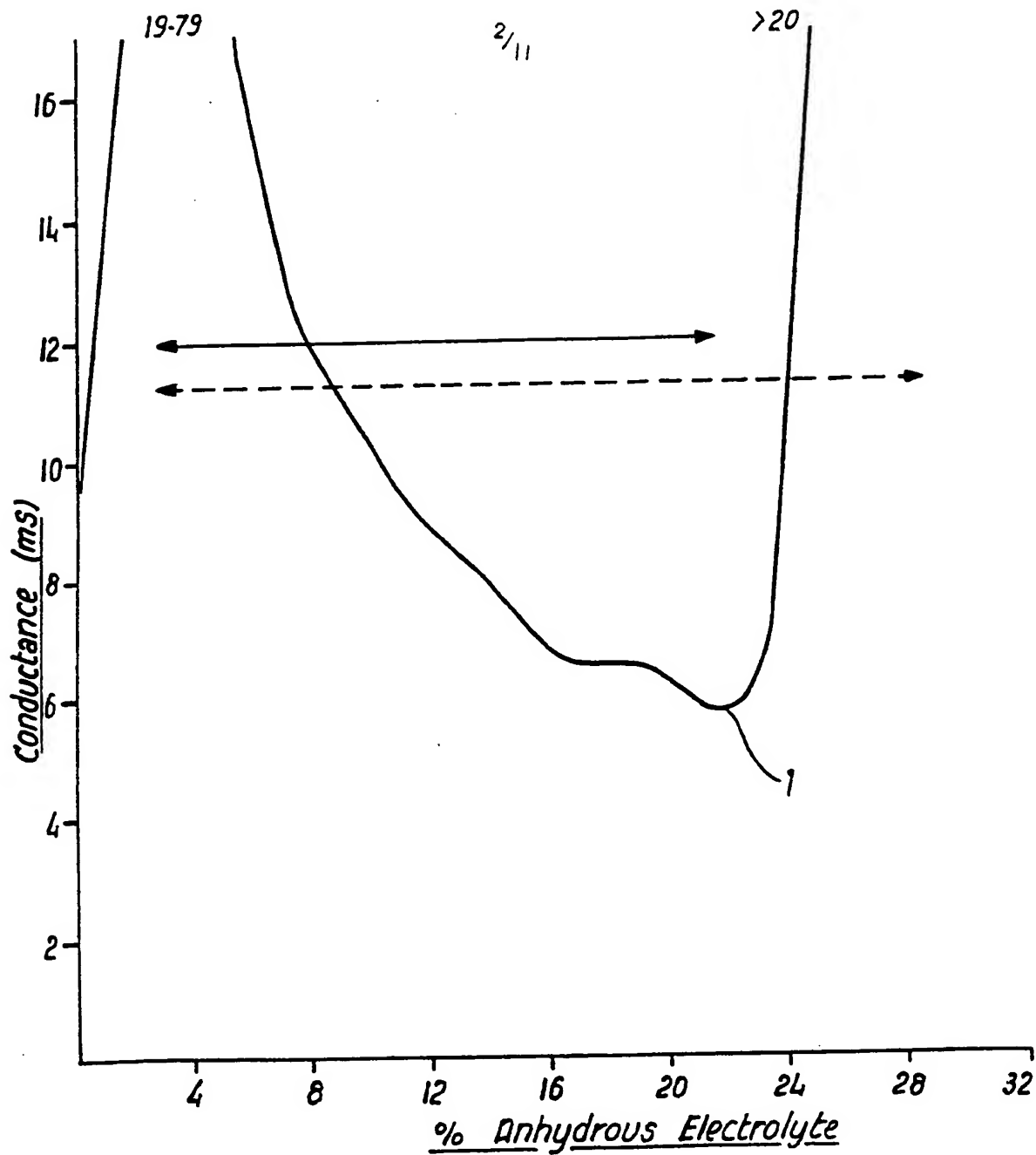
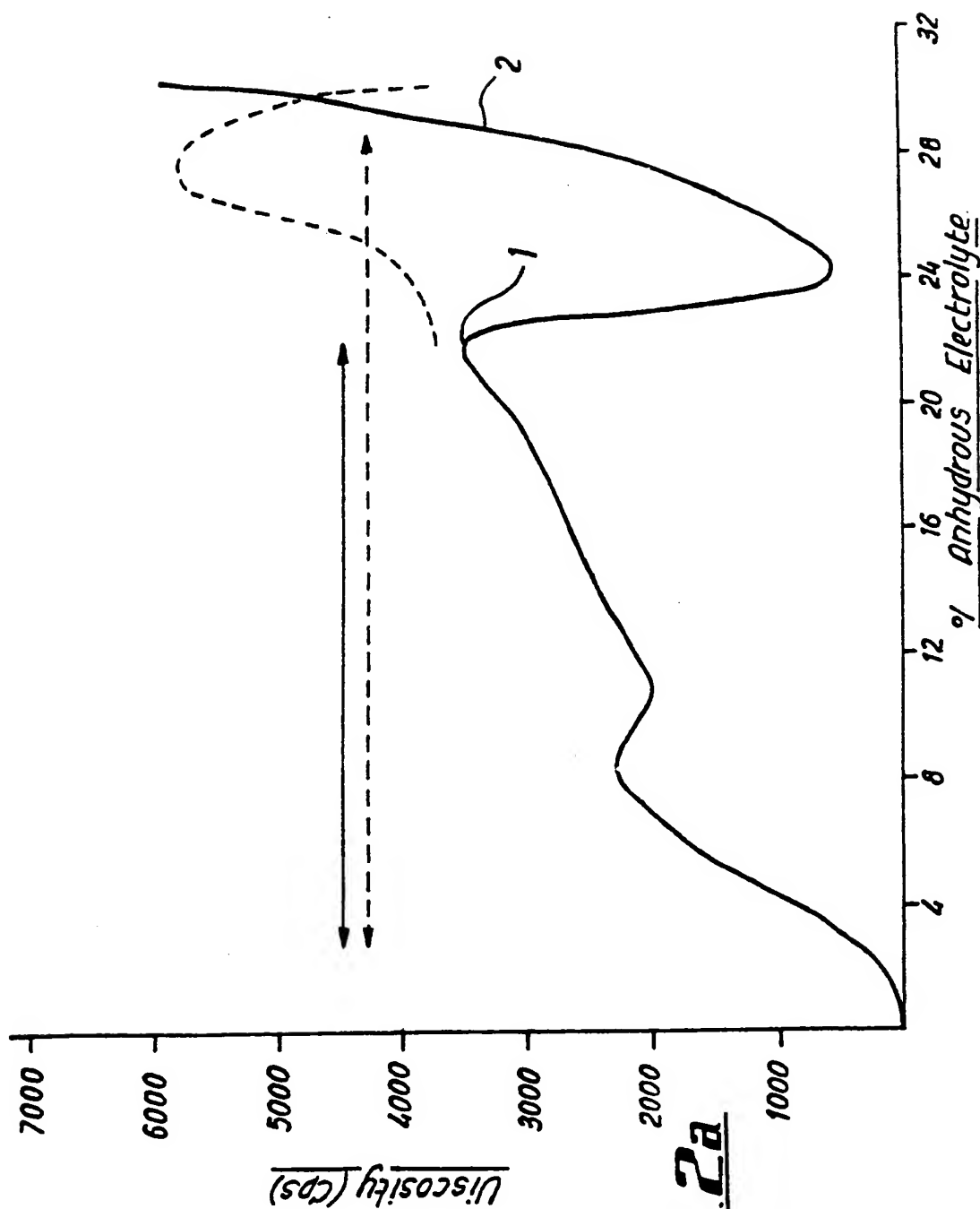


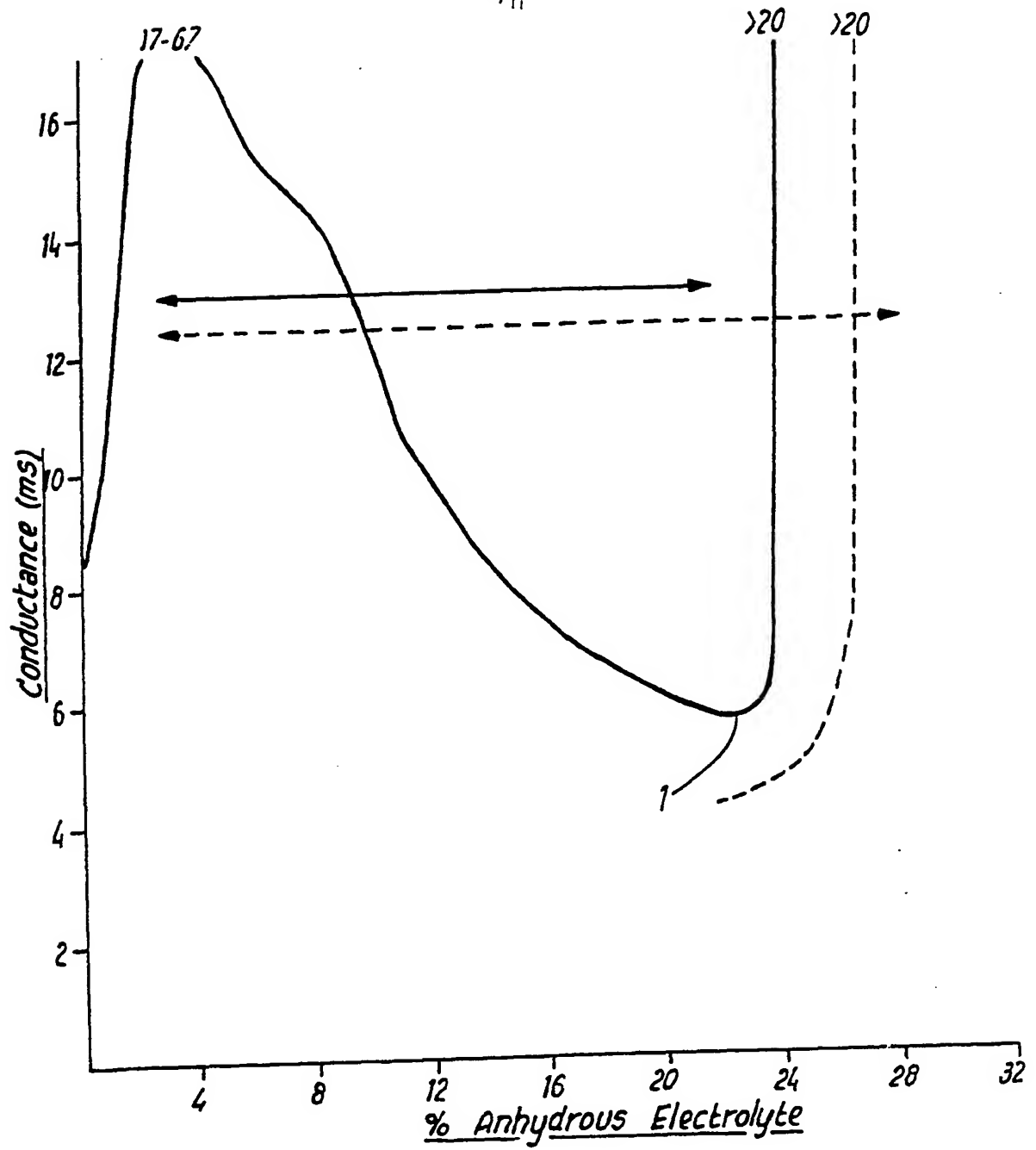
Fig. 1b

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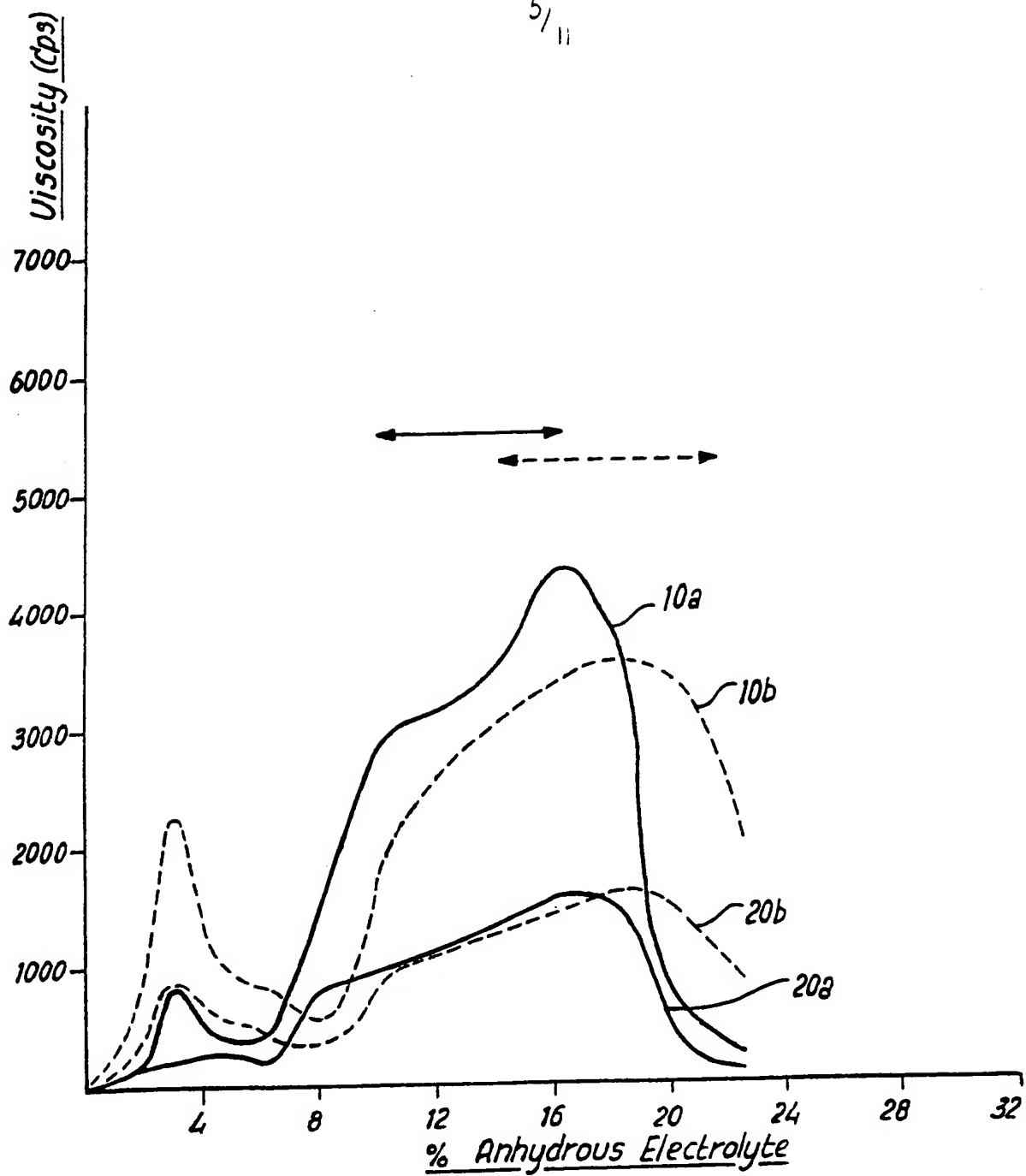


**Fig. 2a**

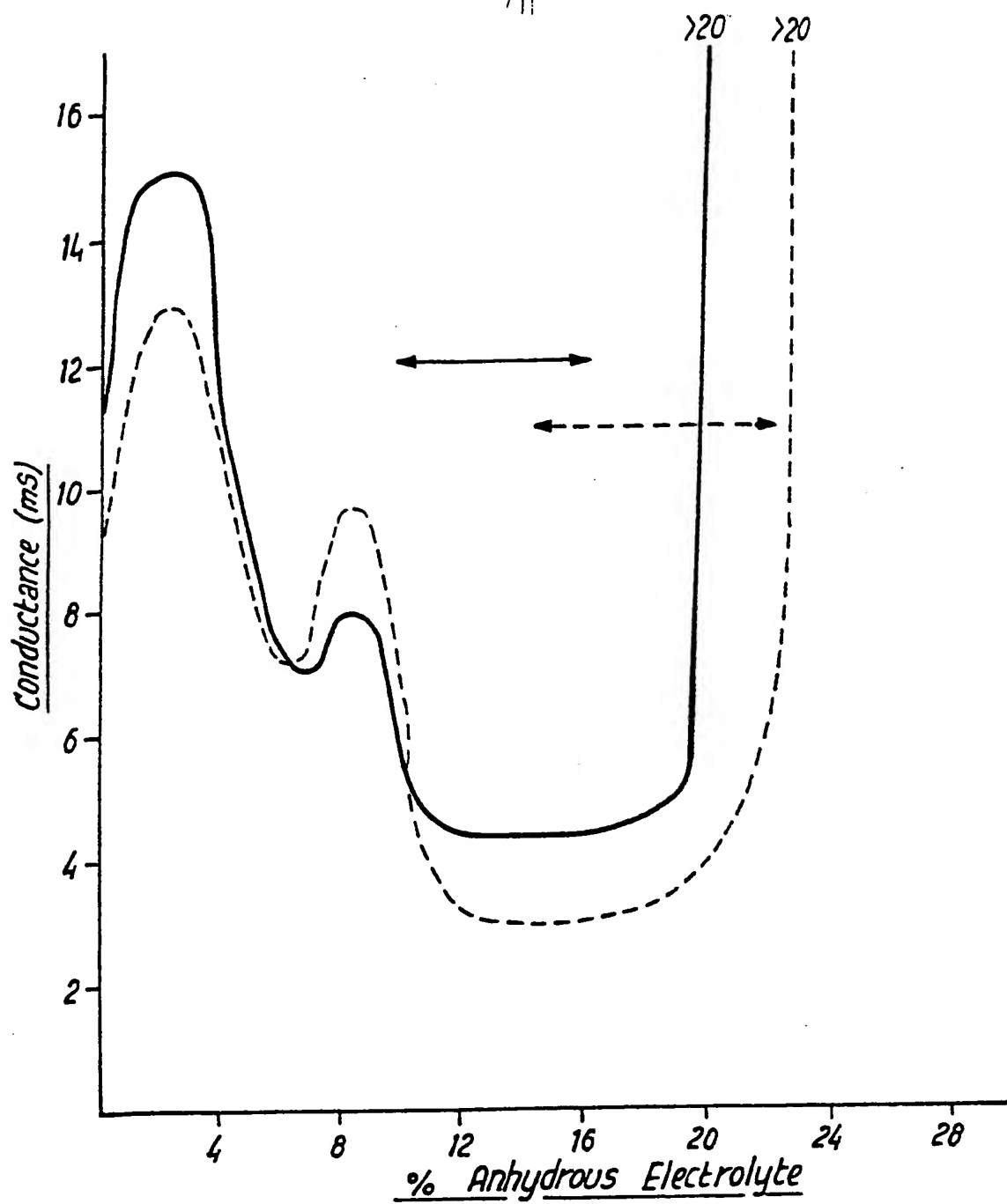
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Fig. 2b

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Fig. 3a

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**Fig. 3b**

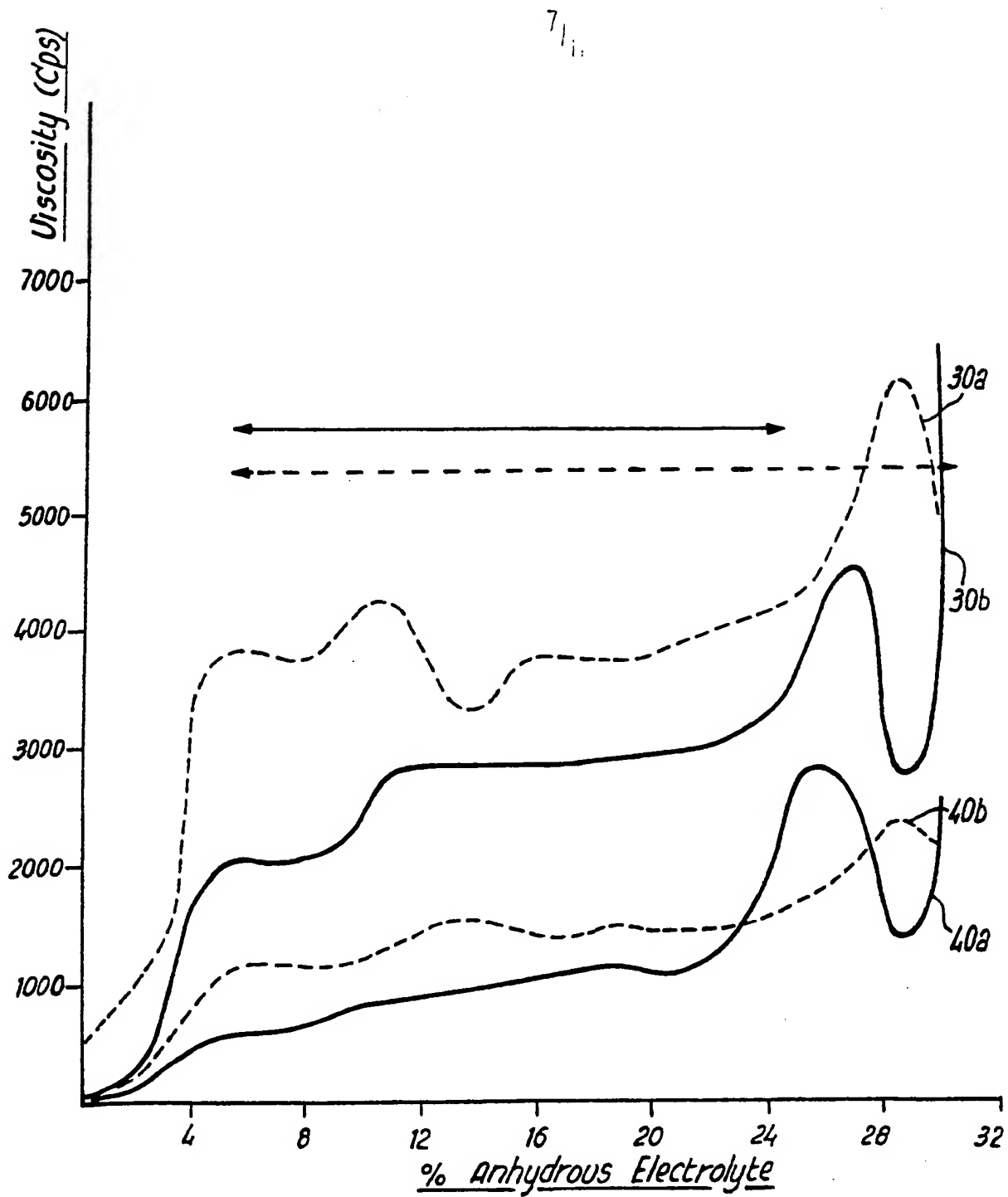
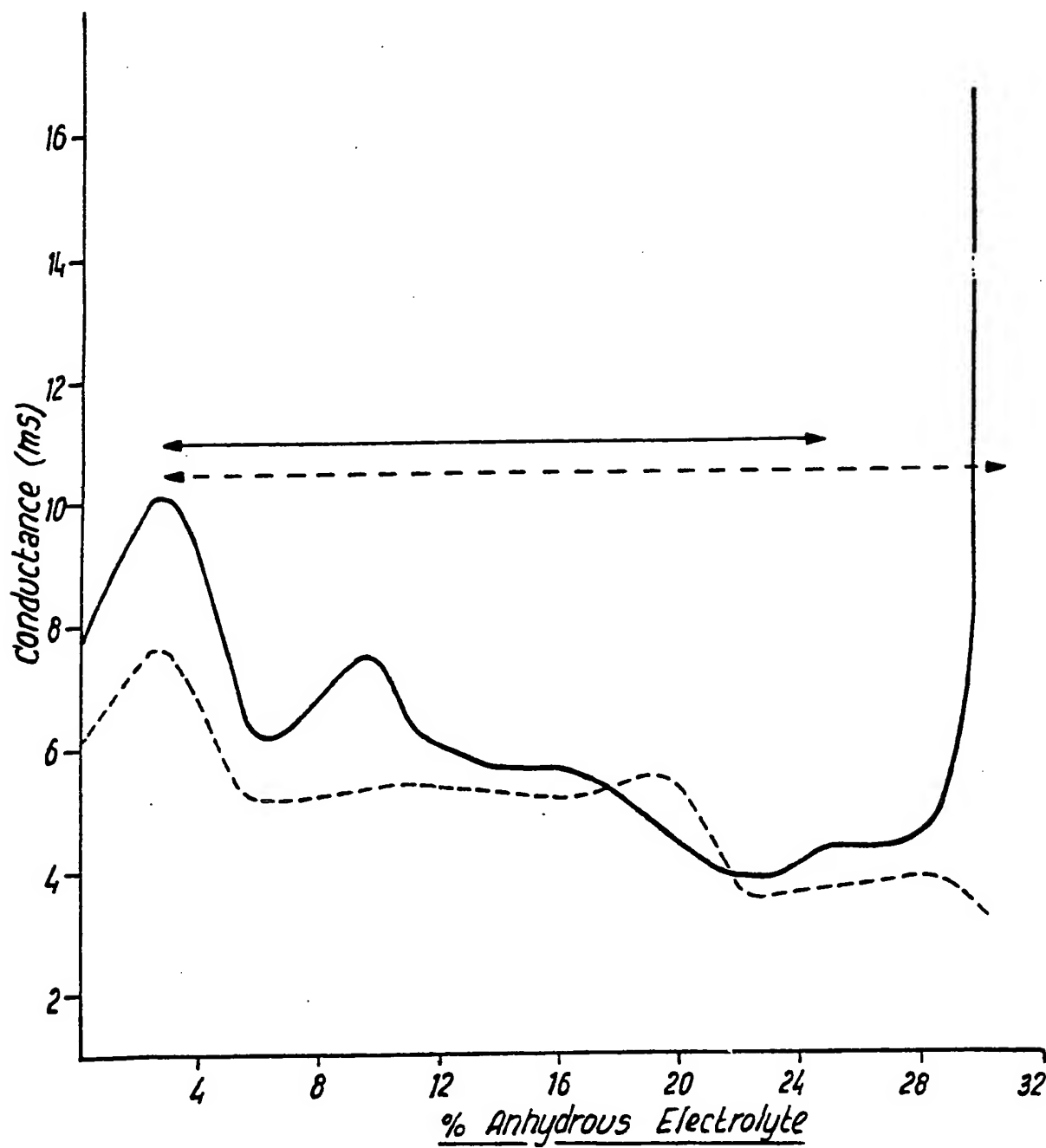


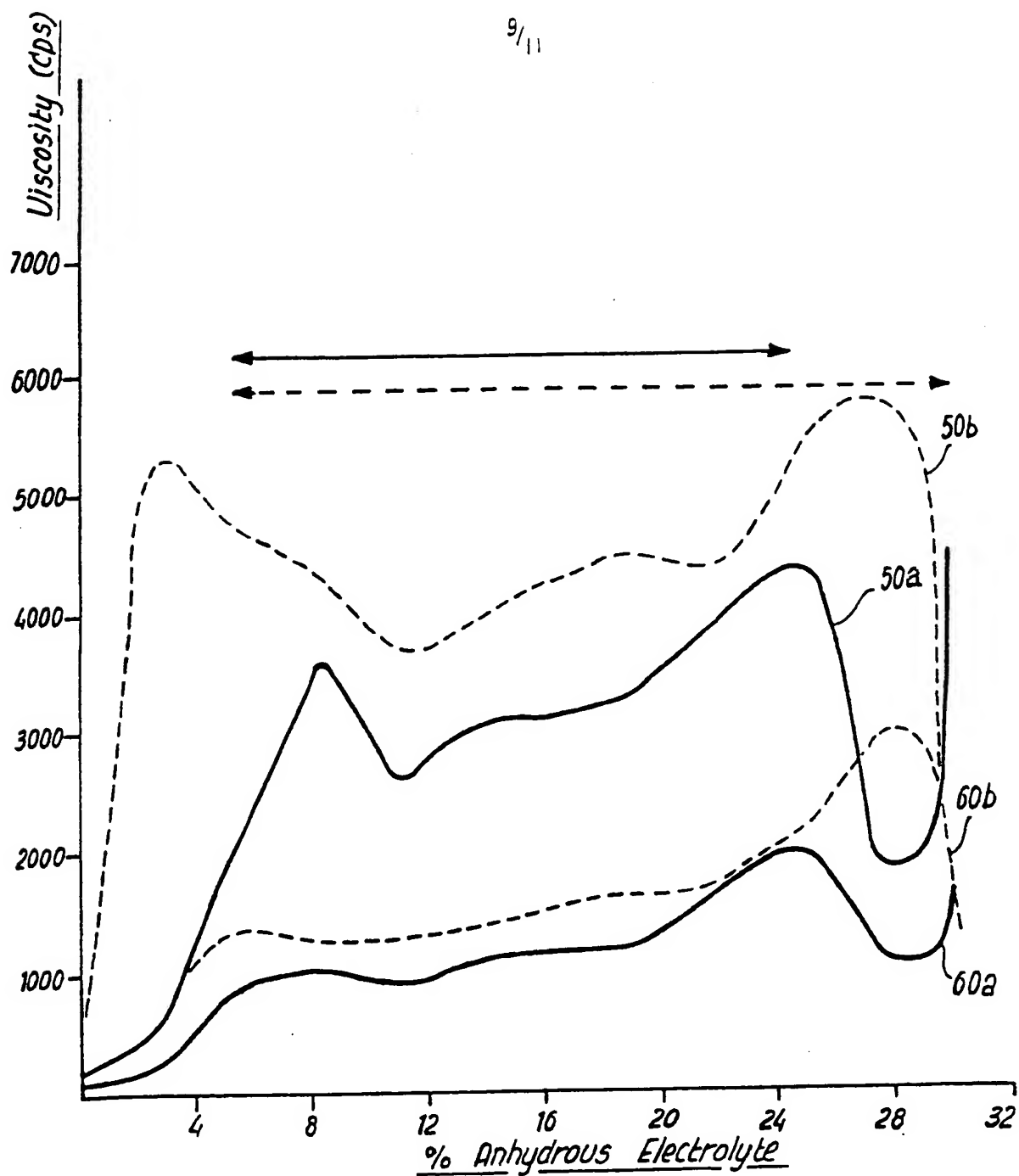
Fig. 4a



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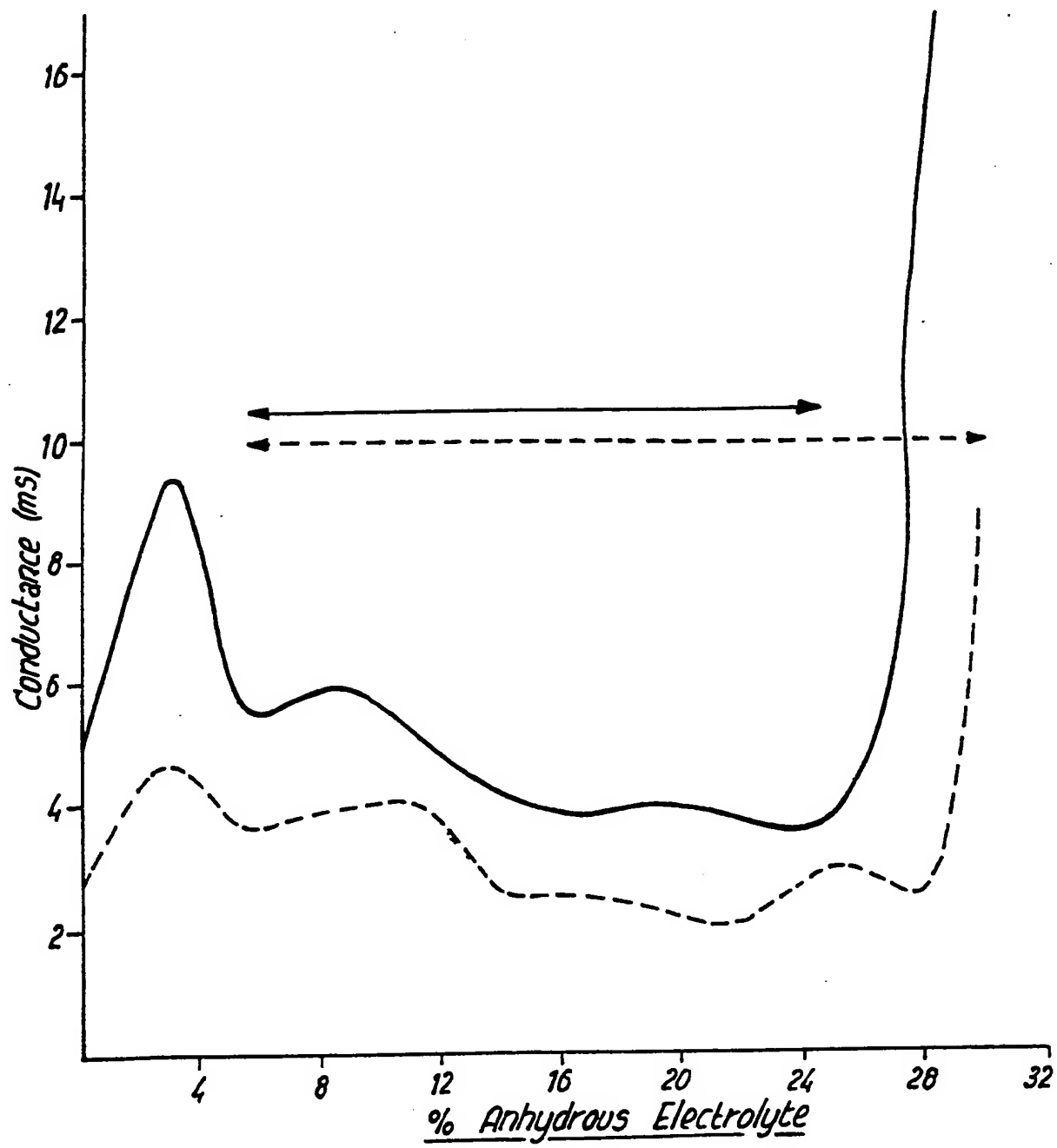
**Fig. 4b**

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**FIG. 5a**

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**Fig. 5b**

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Fig. 6

DETERGENT COMPOSITION

This invention relates to detergent compositions particularly but not exclusively to heavy duty cleaning compositions suitable for domestic use.

5           In order for heavy duty fabric washing compositions to be effective high loads of builders such as alkali metal salts of phosphates, carbonates, silicates, nitrilotriacetates, polymeric polycarboxylates and zeolites must be present. It is  
10 common for formulations of this type to contain a blend of several of these builders, some of which may be present at concentrations above their solubility limits. Where this is the case the undissolved solid material needs to be maintained in suspension to  
15 prevent sedimentation.

The suspending system has previously been provided by interacting a surfactant blend with electrolyte to achieve "internally" structured systems. Here, the dissolved electrolyte causes the  
20 surfactant molecules to arrange themselves into either spherulitic flocs, as described in GB 2153380 or a lamellar phase as described in EPA 0086614. lamellar phase compositions generally contain higher levels of electrolyte than systems containing spherulitic flocs.

At intermediate levels of electrolyte unstable compositions are obtained.

It is an object of this invention to deal with this problem, by incorporating an "external"  
5 stabilising or structuring agent into the compositions.

According to the invention there is provided a detergent composition comprising a builder, surfactant and an electrolyte characterised in that the unstable combination of said builder, surfactant and electrolyte  
10 is stabilised by the addition of a stabilising agent.

In a preferred embodiment of the invention the stabilising agent is a mineral silicate.

In a further preferred embodiment of the invention the stabilising agent is a bentonite clay.

15 One method of identifying the intermediate level of electrolyte giving rise to unstable compositions as referred to in the invention, is to measure the changes in conductivity and viscosity of the surfactant system with increasing electrolyte  
20 concentration. This "intermediate" region may be described as follows:-

As the electrolyte concentration is increased from a first point the conductivity approaches a minimum value and the viscosity approaches a maximum value. Further addition of a solubilised electrolyte such as sodium hydroxide, nitrilotriacetate or ethylenediamine tetra-acetate causes a drop in viscosity and may cause a further drop in conductivity but more usually results in a marginal rise in conductivity. At this stage storage of the compositions at temperatures below 3°C and at 35°C leads to the separation of the compositions into two phases. This usually occurs after three to five days of storage. A still further small addition of electrolyte results in a marked reduction in the viscosity of the composition and a considerable increase in conductance. These compositions usually separate into two phases after storage at temperatures below 3°C and at 35°C for twelve hours to three days. Continued addition of electrolyte causes the viscosity of the composition to rise rapidly and this is probably the onset of the lamellar phase and, therefore, the end of the "intermediate" region. Lamellar compositions also tend to be unstable on storage.

We have discovered that by the addition of a stabilising agent such as a mineral silicate for example bentonite products comprising this "intermediate" electrolyte concentration which have previously proven unstable can be stabilised.

The composition of the invention may comprise the following ingredients:-

Any suitable surfactant system may be used with preferably from 25% to 35% of the surfactant system being present as insoluble nonionic ingredients. For example anionic surfactants such as alkyl benzene sulphonate in the concentration range from 6% to 12% by weight of the total composition blended with a nonionic surfactant, the nonionic surfactant having a hydrophile-lipophile balance (HLB) of less than ten and preferably less than eight. Suitable nonionic surfactants comprise alcohol ethoxylates with carbon chain lengths of from ten to sixteen with a mean average of 3 moles of ethylene oxide per mole of alcohol. The preferred concentration range of the nonionic surfactant is in the range from 2% to 6% by weight of the total composition and more preferably from 2% to 4% by weight of the total composition. Low foaming ethylene oxide and propylene oxide block copolymers may be included in the composition in a preferred concentration range from 0.5% to 4% by weight of the total composition and more preferably from 1% to 2% by weight of the total composition. Other examples of nonionic surfactants that may optionally be included are amines and amine oxides more preferably of the ethoxylated type. The



preferred carbon chain length of the amines and amine oxides is from fourteen to eighteen.

5 The above described surfactant system is preferably in the concentration range from 5% to 25% by weight of the total composition and more preferably from 10% to 15% by weight of the total composition.

10 Any suitable glycol ether may be included such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether.

15 The preferred concentration range of the glycol ether is in the range from 1% to 8%, preferably from 2% to 6% and more preferably from 2% to 4%.

The composition may comprise hydrotropes such as ethanol, xylene sulphonate, and cumene sulphonate.

20 The preferred concentration range of the hydrotrope is less than 2% by weight of the total composition.

The composition may comprise builders alone or in combination such as phosphonates, phosphates for example sodium tripolyphosphate, sodium carbonate, sodium bicarbonate, sodium silicates and sodium  
5 nitrilotriacetate. other examples of builder include ethylene diamine tetra acetate but this is not a favoured ingredient as it is environmentally undesirable. It has been found that polycarboxylic acids destabilise the compositions and as a result are  
10 not considered to be desirable ingredients.

The preferred concentration range of builder is from 7% to 32% by weight of the total composition.

The composition may also include the following: dyes, antiredeposition agents such as sodium carboxy  
15 methyl cellulose, optical brighteners and antifoaming agents.

The concentration range of any dye, anti-redeposition agent, optical brightener and anti-foaming agent may be varied as required.

20 Any suitable stabilising agent such as a mineral silicate may be used for example sepiolite which comprises minute bundles of hollow needle like crystals of magnesium silicate. Other examples include hectorite minerals, calcium bentonites, sodium

bentonites, attapulgite and smectite.

The preferred stabilising agents such as bentonites are those having a greater swellability in solutions of sequestrants than in water alone. For  
5 each sequestrant, other than polycarboxylates, there is also a concentration at which sedimentation of the bentonite is completely prevented.

To determine swellability, a dispersion in water containing 2.5% bentonite is stirred vigorously for 5  
10 minutes. The solution is left to settle for 60 hours and the height of the sedimented bentonite (h) and the combined height (H) of the sedimented bentonite plus aqueous phase are taken. The percentage swellability (%S) can then be calculated from:

15 
$$\%S = h/H \times 100$$

The procedure is repeated in the presence of sequestrant using a concentration range of 0.5% to 5% of sequestrant in 0.5% increments. Within this range, most bentonite dispersions should show a greater  
20 percentage swellability than for bentonite dispersed in water alone.

The preferred concentration of the stabilising agent is in the range from 1% to 8% by weight of the total composition and more preferably 2% to 5% by weight of the total composition.

5           The invention will now be described further by way of example with reference to the accompanying drawings in which:-

10           Figs.1a to 5a show the variation of the viscosity of various surfactant systems with increasing electrolyte concentration;

          Figs.1b to 5b show the variation of the conductance of various surfactant systems with increasing electrolyte concentration;

15           Fig.6           is an electronmicrograph of one composition of the invention at 6000 times magnification.

          Unless otherwise specified the continuous line in the drawings 1a to 5b represents the variation in the measured property with increasing electrolyte

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concentration of a detergent composition which does not comprise a stabilising agent such as a mineral silicate and the dotted line represents the variation in measured property with increasing electrolyte concentration of a detergent composition comprising a mineral silicate. The horizontal continuous and dotted lines represent the stability range of the compositions not comprising mineral silicate and the composition comprising mineral silicate respectively. In the examples the equipment used for the measurement of viscosity was a Poulton, Selfe & Lee: Model LU8 viscometer and the equipment used for the measurement of conductivity was a Bibby SMCi conductivity meter.

EXAMPLE

15	<u>System A</u>	<u>Active Ingredient</u>	<u>% wt</u>
		Alkyl benzene sulphonate	8.00
		Amine oxide	0.25
		Alcohol ethoxylate	2.00
		Alcohol EO/PO copolymer	2.00
20		Ethyl digol	2.00
		Water	) to 100
		Electrolyte	)

Viscosity: Speed 12 Spindle 4

Conductivity meter: Cell Constant 1.0

The variation in viscosity and conductance of System A over a range of anhydrous electrolyte content was measured under the above listed test conditions. The results of the experiment are illustrated in  
5 Figs.1a and 1b.

Referring now to Figs.1a and 1b it can be seen that from 22% to 30% anhydrous electrolyte the viscosity of the composition passes through a minimum and subsequently rises whilst conductivity, which is  
10 directly proportional to the measured conductance, increases rapidly and remains at a relatively high value. The compositions which comprise the "intermediate" proportion of electrolyte as illustrated in the viscosity trough are unstable on storage at  
15 temperatures from below 5°C to 35°C.

By adding a stabilising agent of the invention which in the example is the mineral silicate bentonite the products in this region of instability are found to be stabilised. In this example the stabilisation is  
20 accompanied by an increase in measured viscosity to a maximum value which is in turn followed by a decrease in measured viscosity. The effect of the addition of the stabilising agent is illustrated by the dotted line in Fig.1a.

Fig.1b shows how the conductivity of System A varies with the addition of electrolyte, the System A exhibiting a small degree of alkalinity. System A is found to be stable in the electrolyte content range from 2.5% to 22.0% beyond which instability occurs. Addition of the stabilising agent bentonite to the System A system extends the region of stability to substantially 29% electrolyte content.

#### EXAMPLE 2

The experimental procedure of Example 1 was followed using System A as the surfactant system. However, the degree of alkalinity exhibited by the system was reduced, a mixed sequestrant system of nitrilotriacetate and sodium tripolyphosphate being used, experiment was carried out under the following test conditions:-

Viscometer: Speed 12 Spindle 4

Conductivity meter: Cell Constant = 1.0

The results of the example are illustrated in Figs.1a and 1b.

The addition of the stabilising agent bentonite to the composition results in an increase in the stability range of the composition from a previous upper

stability limit of 22% anhydrous electrolyte content to substantially 28.8% anhydrous electrolyte content.

EXAMPLE 3

	<u>System B</u>	<u>Active Ingredient</u>	<u>% wt</u>
5		Alkyl benzene sulphonate	9.0
		Ethyl digol	4.0
		Phosphonate (a.i.)	1.00
		Alcohol ethoxylate	3.00
		Water	)to
10		Electrolite	)100

Viscometer: Low Shear Speed 12 Spindle 4

High Shear Speed 60 Spindle 4

Conductivity meter: Cell Constant = 1.0

15 The experimental procedure of Example 1 was followed using System B in place of System A. The experimental procedure was carried out at both low shear (10) and high shear (20) under the above listed test conditions.

20 One of the electrolytes of the electrolyte blend of System B was highly soluble. A sequestrant system comprising nitrilotriacetate was used.



The results of the experiment are illustrated in Figs.3a and 3b.

Referring now to Figs.3a and 3b the viscosity curve is seen to exhibit a much more shallow trough when compared to the previous examples. The resulting lower viscosity due to the application of high shear is due to the collapse of the lattice structured network.

The stability range of the compositions is seen to increase from a previous upper limit of substantially 16.5% anhydrous electrolyte content to substantially 22% anhydrous electrolyte content on addition of the stabilising agent bentonite.

EXAMPLE 4

	<u>System C</u>	<u>Active Ingredient</u>	<u>% wt</u>
15		Alkyl benzene sulphonate	8.00
		Ethyl digol	2.00
		Amine oxide	0.25
		Alcohol ethoxylate	3.00
		Water	)to
20		Electrolyte	)100

Viscometer: Low viscosity Speed 12 Spindle 4

High viscosity Speed 60 Spindle 4

Conductivity Meter: Cell Constant = 1.0

The experimental procedure of Example 1 was followed using System C in place of System A both at low shear (30) and high shear (40) under the above listed test conditions. A mixed sequestrant system comprising nitrilotriacetate and sodium tripolyphosphate was used. The results of the experiment are illustrated in Figs.4a and 4b.

Referring now to Figs.4a and 4b it can be seen that the stability range of the System C composition is increased from a previous upper limit of electrolyte content at 24.8% to a new upper stability limit of 30.8% owing to the addition of the stabilising agent bentonite.

#### EXAMPLE 5

15	<u>System D</u>	<u>Active Ingredient</u>	<u>% wt</u>
		Alkyl benzene sulphonate	8.00
		Ethyl digol	2.00
		Amine oxide	0.25
		Alcohol ethoxylate	2.00
20		Alcohol EO/PO copolymer	1.00
		Amine (a.i.)	2.00
		Water	) to
		Electrolyte	) 100

Viscosity: Low Viscosity Speed 12 Spindle 4

High Viscosity Speed 60 Spindle 4

Conductivity meter: Cell Constant = 1.0

5 The experimental procedure of Example 1 was followed using System D in place of System A under the above listed reaction conditions. A mixed sequestrant system comprising nitrilotriacetate and sodium tripolyphosphate. The results of the experiment are illustrated in Figs.5a and 5b.

10 Referring now to Figs.5a and 5b it can be seen that the stability range of the System D composition has been increased from a previous upper percentage electrolyte limit of 24.6% to 30.2%.

15 In summary, referring now to Figs.1a to 5b the experimental results exhibit the following characteristics:-

1. A sudden reduction in viscosity accompanied by a rise in conductivity at which point compositions not containing a mineral silicate become unstable.
- 20 2. Where compositions not containing mineral silicates show a viscosity trough, addition of a mineral silicate changes the viscosity trough into a viscosity peak, which is particularly marked when

viscosity is measured at low shear rates.

3. Addition of a mineral silicate extends the electrolyte level over which stable compositions are obtained.

5 4. The effective increase in stability range is limited to less than eight percent (8%) additional electrolyte.

10 5. Addition of mineral silicate to unstable compositions reduces their conductivity from typically greater than 20 milli Siemens to less than six milli Siemens, though stable compositions containing mineral silicates can have conductivities greater than 15 milli Siemens.

15 6. Each of the viscosity curves show a maximum viscosity immediately prior to plunging to a viscosity minimum.

20 7. The viscosity maximum of the compositions containing mineral silicate is at a level of electrolyte 2% to 4% greater than the maximum obtained in the absence of mineral silicate.

8. Addition of mineral silicate to stable base compositions and to unstable compositions lying in the

viscosity trough causes their conductances to be reduced.

9. Three of the four systems tested showed a minor first conductivity minimum at approximately 6% anhydrous electrolyte.
- 5

Referring to Fig.6 there is shown an electromicrograph of one composition of the invention. The photograph shows large particles of mineral silicate referenced 70 surrounded by the surfactant builder and electrolyte mixture. No spherulitic flocs are present nor is any lamellar structure observable. Thus the photograph further confirms that the composition is in the intermediate electrolyte range.

10

It is to be understood that the above listed examples are by way of illustration only and that many modifications may be made without departing from the spirit of the invention.

15

CLAIMS

1. A detergent composition comprising a builder, a surfactant and an electrolyte, characterised in that the unstable combination of said builder, surfactant and electrolyte is stabilised by the addition of a stabilising agent.
2. A detergent composition as claimed in Claim 1, wherein the stabilising agent is a mineral silicate.
3. A detergent composition as claimed in claims 1 or 2, wherein the stabilising agent comprises a bentonite clay.
4. A detergent composition as claimed in any preceding claim, wherein the stabilising agent comprises any of the following: sepeolite, magnesium silicate, hectorite, calcium bentonite, sodium bentonite, attapulgite or smectite.
5. A detergent composition as claimed in any preceding claim, wherein the stabilising agent has a greater swellability in a solution of sequestrant than in water alone.
6. A detergent composition as claimed in any preceding claim, wherein the concentration of the stabilising agent is in the range from 1 to 8 percent by weight of the total composition.
7. A detergent composition as claimed in any preceding claim, wherein the concentration of the

stabilising agent is in the range from 2 to 5 percent by weight of the total composition.

8. A detergent composition as claimed in any preceding claim, wherein the electrolyte concentration  
5 comprises the range defined between a first value in which the conductivity of the builder, surfactant and electrolyte combination approaches a minimum value and the viscosity thereof approaches a maximum value and a second value of substantially the same viscosity as  
10 the first value.

9. A detergent composition as claimed in any preceding claim, wherein the electrolyte concentration is in the range from 16 to 31 percent by weight of the total composition.

15 10. A detergent composition as claimed in any preceding claim, wherein the electrolyte concentration is intermediate that necessary to cause the surfactant to be present as spherulitic flocs and lamellar phase.

11. A detergent composition as claimed in any  
20 preceding claim, wherein from 25 to 35 percent by weight of the surfactant system is present as nonionic ingredients.

12. A detergent composition as claimed in any preceding claim, wherein the surfactant comprises  
25 anionic surfactants in the concentration range from 6 to 12 percent by weight of the total composition and

a nonionic surfactant.

13. A detergent composition as claimed in claims 11 or 12, wherein the nonionic surfactant has a hydrophile-lipophile balance of less than 10.

5 14. A detergent composition as claimed in claims 11, 12, or 13, wherein the nonionic surfactant has a hydrophile-lipophile balance of less than 8.

15. A detergent composition as claimed in any preceding claim, wherein the surfactant comprises  
10 alcohol ethoxylates with carbon chain lengths in the range from ten to sixteen; ethylene oxide or propylene oxide copolymers; amines, amine oxides, ethoxylated amines or ethoxylated amine oxides.

16. A detergent composition as claimed in any of  
15 claims 11 to 15, wherein the nonionic surfactant is in the range from 2 to 6 percent by weight of the total composition.

17. A detergent composition as claimed in any of claims 11 to 16, wherein the nonionic surfactant is  
20 in the range from 2 to 4 percent by weight of the total composition.

18. A detergent composition as claimed in any preceding claim, wherein the total surfactant concentration is in the range from 5 to 25 percent by  
25 weight of the total composition.

19. A detergent composition as claimed in any



preceding claim, wherein the total surfactant concentration is in the range from 10 to 15 percent by weight of the total composition.

20. A detergent composition as claimed in any  
5 preceding claim, wherein the builder comprises any of the following: phosphonates, phosphates, sodium tripolyphosphate, sodium carbonate, sodium bicarbonate, sodium silicate, sodium nitrilotriacetate or ethylene diamine tetra acetate.
- 10 21. A detergent composition as claimed in any preceding claim, wherein the builder comprises from 7 to 32 percent by weight of the total composition.
22. A detergent composition as claimed in any preceding claim comprising glycol ether.
- 15 23. A detergent composition as claimed in any preceding claim comprising any of the following: ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol  
20 monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether.
24. A detergent composition as claimed in claims 22  
25 or 23, wherein the glycol ether is in the range from 2 to 6 percent by weight of the total composition.

25. A detergent composition as claimed in any preceding claim comprising any of the following: hydrotrope, anti-redeposition agent, optical brightener or anti-foaming agent.